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THE ROLE OF RADIATIVE ENERGY IN COMBUSTION PROCESSES

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THE ROLE OF RADIATIVE ENERGY IN COMBUSTION PROCESSES

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 Submitted 21 April 1950

## 1. DISTRIBUTION OF RADIATIVE AND KINETIC ENERGY AMONG CARRIERS

Radiation absorbing molecules in gaseous inflammable mixtures irradiated from a suitable source may on account of absorption of radiative energy get excited to the energy level required for combustion. When excited molecules collide with other molecules, new molecules form after complicated structural changes which are accompanied by the release of light and heat.

The reinforced thermal motion of molecules with local liberation of heat from the combustion reaction multiplies the number of molecules in the mixtures that are able to activate other molecules of the burning mixture. Thus we may assume that combustion is initially excited by radiative energy.

To evaluate the role of radiative energy in the excitation of molecules, let us first examine for thermodynamic equilibrium the comparative distribution of radiative and kinetic energies among their vectors, or carriers.

According to Plank's law, the volumetric density of radiative energy at radiation frequency  $\nu$  (spectral radiation) at thermal equilibrium is

$$U_\nu = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} \quad (1)$$

where  $h = 6.624 \times 10^{-27}$  erg.sec is Plank's constant,  $c = 299,776 \times 10^6$  m/sec is the velocity of light,  $k = 1.38 \times 10^{-16}$  erg/grad is Boltzmann's constant, and  $T$  is the temperature in °K.

The volumetric density of thermal radiation for all frequencies (integral radiation) is

$$U_0 = \int_0^\infty U_\nu d\nu = \frac{8\pi^5 k^4}{15c^3 h^3} T^4 \quad (2)$$

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The number of photons with a radiation frequency between  $\nu$  and  $\nu + d\nu$  per unit volume is found from

$$N_\nu d\nu = \frac{U_\nu d\nu}{(h\nu)} = \frac{8\pi\nu^2}{c^3} \frac{1}{e^{h\nu/kT} - 1} d\nu \quad (3)$$

The total number of photons at thermal equilibrium for all radiation frequencies (over the whole spectrum) per unit volume is found by integration:

$$N_0 = \int_0^\infty \frac{8\pi\nu^2}{c^3} \frac{1}{e^{h\nu/kT} - 1} d\nu = 2.404 \frac{8\pi k^3 T^3}{c^3 h^3} \quad (4)$$

It is of interest to compare at a given moment and for various temperatures the number of photons per unit volume at thermodynamic equilibrium with the number of gas molecules in the same volume at  $p = 1$  atm. The result is presented in Table 1 (see Table 1, app).

Therefore the number of carriers of radiative energy present at each instant per unit volume at thermodynamic equilibrium turns out to be several million times less than the number of molecules per unit volume. But it should be kept in mind that the velocity of light particles is nearly a million times higher than the velocity of molecular motion.

The average energy of a photon is

$$\bar{\epsilon}_{ph} = \frac{U_\nu}{N_\nu} = \frac{\int \nu U_\nu d\nu}{\int \nu N_\nu d\nu} \approx 2.7kT \quad (5)$$

In comparison with the average kinetic energy of moving molecules  $\epsilon_M = \frac{3}{2} kT$  the average quantum energy of thermal radiative equilibrium is twice higher.

The number of quanta with energy  $E_\nu$  (in kcal/mol) among their total number will be

$$\frac{\Delta N_\nu}{N_\nu} = \frac{0.16}{E_\nu} \frac{\left(\frac{E_\nu}{RT}\right)^3}{e^{E_\nu/RT} - 1} \Delta E_\nu \quad (6)$$

where  $R = 1.985$  kcal/kg.mol.deg is the gas constant.

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As seen from this equality a unit volume has few quanta with very high or very low energy. The curve describing distribution of energy of quanta at thermal radiative equilibrium follows the usual distribution curves encountered in statistics.

In contrast to the distribution curve of energy quanta, the distribution curve of molecules with energy  $E_1$  per unit volume of the gas is given by the following equation

$$\frac{\Delta N_{E_i}}{N_0} = \frac{1.128}{E_i} \left( \frac{E_i}{RT} \right)^{3/2} e^{-E_i/RT} \Delta E_i \quad (7)$$

The position of the maximum of the distribution curve of quanta of radiative energy is found from equation (6)

$$\left( \frac{E_i}{RT} \right)_{max} = 2 \left( 1 - \frac{1}{e^{E_i/RT}} \right)$$

and the position of the maximum in the distribution curve of molecular energy is

$$\left( \frac{E_i}{RT} \right)_{max} = \frac{1}{2}$$

By comparing the positions of the maxima of both distribution curves one finds that the distribution curve of energy quanta is shifted towards energies of higher levels. Thus under conditions of thermal equilibrium of gas the relative number of quanta with energies higher than  $E_i$  per unit volume of gas is much higher than the relative number of molecules possessing the same energy level.

Figure 1 represents the distribution curves of kinetic energy of gas molecules and quanta of radiative energy per unit volume at various temperatures, from which it may be seen that the position of the maximum of the distribution curve shifts towards the side of higher energies with rising temperatures.

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If we designate the relative number of quanta having an energy  $E_v$  radiative equilibrium by  $n_{E_v}$  and relative number of molecules with energy  $E_i$  by  $n_{E_i}$ , then according to equations (6) and (7) the ratio

$$\frac{n_{E_v}}{n_{E_i}} = 0.369 \frac{E_i}{E_v} \frac{\left(\frac{E_v}{RT}\right)^3 e^{E_i/RT_{mol}}}{\left(e^{E_v/RT_{ray}} - 1\right) \left(\frac{E_i}{RT_{mol}}\right)^{1/2}}$$

where  $T_{ray}$  and  $T_{mol}$  are respectively "radiative" and "molecular" equilibrium temperatures. In the case of thermodynamic equilibrium both temperatures  $T_{ray}$  and  $T_{mol}$  coincide.

In the case of thermodynamic equilibrium we may also compare the relative numbers of quanta of radiative energy and molecules with energies respectively above  $E_v$  and  $E_i$ .

According to equations (3) and (4) the relative number of quanta having energy above  $E_v$  will be

$$n_{>E_v} = \frac{N_{>E_v}}{(N_v)_{\gamma}} = 0.416 \int_{E_v}^{\infty} \frac{\left(\frac{E_v}{RT}\right)^2 d\left(\frac{E_v}{RT}\right)}{e^{E_v/RT} - 1}$$

Integrating over the region of not too small values of  $E_v$ , we find

$$n_{>E_v} = 0.416 \left[ \left( \frac{E_v}{RT} + 1 \right)^2 + 1 \right] e^{-E_v/RT}$$

As is known the relative number of molecules having an energy above  $E_i$  is

$$n_{>E_i} = \frac{N_{>E_i}}{(N_o)_M} = e^{-E_i/RT}$$

In the case of thermodynamic equilibrium the ratio of these amounts is

$$\frac{n_{>E_v}}{n_{>E_i}} = 0.416 \left[ \left( \frac{E_v}{RT} + 1 \right)^2 + 1 \right]$$

Table 2 represents the ratios  $n_{>E_v}/n_{>E_i}$  and  $n_{>E_v}/n_{>E_i}$  for various equilibria of temperatures ( $T_{ray} = T_{mol}$ ) and for energy  $E_v = E_i = 30\ 200$  kcal/kg.mol (for an example see below) (See Table 2).

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As seen from Table 2 the relative number of quanta having energies above  $E_v = 30,200$  kcal/kg.mol turns out to be much higher than the relative number of molecules having the same energy.

If radiative and molecular equilibria exist separately within a unit volume and if the "radiative" temperature is higher than the "molecular", then the ratio  $n_{E_v} / n_{E_1}$  will be still higher. For example, if  $t_{ray} = 500^\circ$  and  $t_{mol} = 0^\circ$ , then the ratio is  $n_{E_v} / n_{E_1} = 6.77 \cdot 10^{36}$ . Under such circumstances the relative number of quanta having an energy  $E_v = 30,200$  kcal/kg.mol will be many times greater than the relative number of molecules having the same energy. Under the conditions considered also the absolute number of quanta with energy  $E_v = 30,200$  kcal/kg.mol present at a given instant per unit volume will be many times greater than the absolute number of molecules having the same energy. Computation gives the following results.

$$\frac{\Delta N_{E_v}}{\Delta N_{E_1}} = \frac{(N_0)_{qu} n_{E_v}}{(N_0)_M n_{E_1}} = 23.6 \cdot 10^{-10} e^{36} = 10.3 \cdot 10^6$$

The ratio of the absolute number of photons with energy  $E_v$  at any instant in unit volume at  $T_{ray}$ , to the number of molecules at the same energy level  $E_1 = E_v$  present in the same volume at  $T_{mol} < T_{ray}$  and  $p = 1$  atm is

$$\frac{\Delta N_{E_v}}{\Delta N_{E_1}} = 0.757 \cdot 10^{-16} \frac{T_{mol}}{T_{mol}} \frac{E_v}{E_1} \frac{\left(\frac{E_v}{RT}\right)^{3_{mol}} e^{E_v/RT_{mol}}}{\left(e^{E_v/RT_{ray}} - 1\right) \left(\frac{E_1}{RT_{mol}}\right)^{3/2}}$$

For large values of  $E_v = E_1$  this ratio is the higher the more  $T_{ray}$  exceeds  $T_{mol}$ . In this connection it is particularly important to notice that near the heated surface of the gas where  $T_{mol} < T_{ray}$  the number of photons at the high energy level  $E_v$  may exceed many times the number of molecules at the same high energy level. (Footnote: The ratio of the number of photons per unit volume with energy  $E_v = 30,200$  kcal/kg.mol (at  $t_{mol} = 0$ , for various values of  $t_{ray}$ ) to the number of molecules having the same kinetic energy  $E_1$  at  $t_{mol} = 0$  for various values of  $t_{ray}$  is obtained as follows)

$t_{ray} = 0$	100	200	300	400	500°C
$\Delta N_{E_v} / \Delta N_{E_1} = 2.31 \cdot 10^{-9}$	$7.12 \cdot 10^{-3}$	$3.74 \cdot 10$	$1.18 \cdot 10^4$	$5.61 \cdot 10^5$	$10.3 \cdot 10^6$

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Consequently, as shown by the above considerations, photons at high energy levels have relatively higher statistical weight than molecules at the same energy levels.

## 2. ACTIVATION OF MOLECULES IN IRRADIATED BURNING MIXTURES

Although the volumetric density of kinetic energy of molecules is much higher than the volumetric density of radiative equilibrium energy, the probability of energy conversion upon absorption of quanta of radiative energy by molecules not only may be comparable with the probability of energy conversion upon impact of molecules, but may even exceed it considerably. For explanation the following considerations are submitted.

With rising temperature the number of molecules per unit volume of gas decreases and therefore the volumetric density of the inflowing kinetic energy of molecules independently of temperature at atmospheric pressure is

$$U_{\text{mol}} \approx 36.5 \text{ kcal/m}^3.$$

The volumetric density of thermo-radiative equilibrium is found from

$$U_{\text{ray}} = \frac{4.49 \left( \frac{T}{100} \right)^4}{c} \text{ kcal/m}^2$$

Because of the very high velocity of light,  $U_{\text{ray}}$  at ordinary temperatures is many times smaller than  $U_{\text{mol}}$ .

But the intensity of energy conversion within the molecular medium is determined not by the volumetric density of energy, but by the energy flow or its transfer. The molecular energy transfer in gases is determined by the usual equation of heat conduction

$$\vec{q}_{\text{mol}} = -\lambda \cdot \text{grad } T \text{ (kcal/m}^2 \text{ hr)}$$

where  $\lambda$  is the coefficient of molecular thermal conductivity in kcal/m.hr.deg.

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The flow of radiative energy transfer in the absorbing molecular medium, may, as shown in 1948 by the author in his investigation <sup>at (Power, Eng. Trans.)</sup> ~~ANIN~~ be presented in a similar form:

$$\vec{q}_{\text{ray}} = -\frac{1}{3} \frac{1}{K} \cdot \text{grad } c u_{\text{ray}} \quad (\text{kcal/m}^2 \text{ hr})$$

where  $k$  is the coefficient of radiation absorption in units of  $\text{m}^{-1}$ .

For conditions close to local radiative equilibrium  $[c u_{\text{ray}} \approx 4 \times 4.9 \left(\frac{T}{100}\right)^4]$ , the flow of radiative energy transfer may be written in the same form as the molecular transfer

$$\vec{q} = -\lambda_{\text{ray}} \cdot \text{grad } T \quad (\text{kcal/m}^2 \text{ hr})$$

where  $\lambda_{\text{ray}} = \frac{4}{3} \frac{1}{k} \cdot \frac{4 \times 4.9 \left(\frac{T}{100}\right)^4}{T}$  kcal/m hr-deg is the coefficient of radiative thermal conductivity of the medium.

The absorption coefficient  $k$  of a gas is relatively small in comparison with that of a liquid or solid and  $\lambda_{\text{ray}}$  turns out to be much greater than  $\lambda_{\text{mol}}$ . Hence the energy transfer by photons will accordingly be more intensive than the molecular energy transfer.

Figure 2 presents the absorption coefficient  $k$  of water vapor and carbon dioxide versus temperature, at  $p = 1$  atm (average) for all active bands of the spectrum. Figure 3 shows the limit values of the opacity (blackness) coefficients  $\epsilon_{\text{L}} = \infty$  of the same gases for various temperatures.

Figure 4 gives the mean values of coefficients  $\lambda_{\text{ray}}$  of radiative thermal conductivity for  $\text{H}_2\text{O}$  and  $\text{CO}_2$  at  $p = 1$  atm, as computed from the following formula:

$$\bar{\lambda}_{\text{ray}} = \frac{4}{3} \frac{1}{K} \cdot \frac{4 \times 4.9 \left(\frac{T}{100}\right)^4}{T}$$

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As seen from the data of Figure 4, the mean coefficient of thermal conductivity of water vapor appears to be several orders higher than the coefficient of molecular thermal conductivity of this gas. Even carbon dioxide, noteworthy for its high absorption coefficient, possesses good radiative thermal conductivity for sufficiently high temperatures.

It is interesting and important to notice that ~~since~~ the coefficient of molecular energy transfer consists of the product of the mean velocity  $\bar{w}$  of energy carriers of molecules by the mean length  $\bar{l}_M$  of their free path (the coefficient of molecular transfer or diffusion is  $D_M = \frac{1}{3} \bar{w} \bar{l}_M \text{ m}^2/\text{hr.}$ ), and the coefficient of radiative energy transfer ( $D_r = \frac{1}{3} c \bar{l}_{ph} \text{ m}^2/\text{hr.}$ )

consists of the product of the velocity of light  $c$  by a factor  $\frac{1}{3}$ , which in this case plays the role equivalent to the mean ~~length~~ of free path of photons ( $\bar{l}_{ph} = 1/k$ ). With such an interpretation of photon energy transfer, justified only under condition of local radiative equilibrium—that is, when total absorption equals radiation ( $kcU_p = k_{\lambda} n I_{\lambda, T}$ ), for a certain absorption coefficient of the medium—one can evaluate the length of free path of the photon. For example, the absorption coefficient  $k_{\lambda}$  (1) is respectively 2, 2.5, and 10 (in units of  $10^{-2} \text{ 1/m}$ ) for bands with wavelengths  $\lambda = 1.42, 1.89, \text{ and } 2.7 \mu$  of the absorption spectrum of water vapor in saturated air at  $t = 25^\circ$  (concentration of water vapor is  $23 \text{ g/m}^3$ ).

With such absorption coefficients of the medium the mean ~~length~~ free path will be 50, 40 and 10 m; that is, the transparency of the air for these rays will be rather high. If the concentration of water vapor were increased 100 fold, then even in this case the mean ~~length~~ free ~~photon~~-path <sup>of a photon</sup> would be respectively 0.5, 0.4, and 0.1 m.

Thus photon transfer in contrast to molecular energy transfer is characterized by much deeper penetration of the energy carriers. Only for very high concentrations of radiation-absorbing molecules (corresponding to

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liquids or solids), or for their corresponding structure, may the mean <sup>of the photon</sup> ~~length of free photon~~ path appear to be sufficiently small.

It should be noted that the distribution of lengths of free photon path corresponds to the equation

$$\frac{N_l}{N_{ph}} = \frac{l/\bar{l}}{e^{l/\bar{l}}}$$

which has a maximum at  $(l/\bar{l})_{max} = 1$ . The curve describing the distribution of lengths of free photon path is shifted towards the shorter lengths  $l/\bar{l}$ , in comparison with the curves describing the energy distribution of photons and molecules. Thus, for example, for  $l/\bar{l} = 1/10$  we have  $N_l/N_{ph} = \frac{1}{9.25}$  (≈9%) and for  $l/\bar{l} = 1/100$  we have  $N_l/N_{ph} = \frac{1}{100}$  (1%).

Consequently a rather considerable number of photons out of their total number possesses short free paths and therefore the probability of encounters of active photons with molecules upon their activation will be quite noticeable, only if the layer of the irradiated gas or its concentration is not too thin.

In order to be convinced of the dominant role of radiative energy transfer through gaseous space, one needs merely to compare thermal conductivity in a flat parallel layer of gas from one heated surface to the other by molecular thermal conductivity and by radiation. Even supplementary convective energy transfer will not be able, in this case, to decrease the main role of radiative energy transfer.

In this connection it is impossible to agree with Hinshelwood who in his monograph "Kinetics of Gaseous Reactions" (?) argues against the radiative theory of activation of molecules in reactions, stating: "Except at very high temperatures the amount of radiation present in a unit volume of gas at normal pressure is very small in comparison with the kinetic and internal energy of gaseous molecules; therefore it seems probable that the activation originates rather by impact than by radiative absorption." Thereafter, however, Hinshelwood writes "The acceleration of chemical reactions under the effect of light shows <sup>that</sup> basically the assumption that molecules are activated by absorption of usual thermal radiation is not unlikely".

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The contradictions of Hinshelwood may easily be due to the fact that the activation of molecules is determined not by the volumetric energy density, but by the flux of active energy carriers. The power of radiative flux at not too low temperatures appears to be higher than the molecular energy flux in the gas.

The considerations outlined by Hinshelwood are connected with criticism of Perrin's assumption (1919) that monomolecular activation of molecules is due to radiative effects on the molecule. In the case of weak concentrations the molecules may be isolated from impacts, but according to this scheme the reaction should proceed with the same relative speed.

$$\frac{dx}{dt} = -Kx$$

where  $x$  is the concentration of the reacting product,  $K$  is the reaction constant.

The role of radiation in activation of molecules may have its origin, we may assume, in the absorption of light quanta at a frequency corresponding to the activation energy. For instance, for the energy of activation of monomolecular decomposition of nitrogen pentaoxide ( $N_2O_5$ )  $E_A = 24\,700$  kcal/kg.mol the active frequency of the infrared spectrum should correspond to  $26.10^{13}$  sec<sup>-1</sup> or  $\lambda = 1.15$  micron<sup>(3)</sup>. A test checking the irradiation effect of vapors of nitrogen pentaoxide by this frequency in a chamber at low pressure did not show an acceleration of the reaction behavior. In this connection Glasston<sup>(3)</sup> remarks: "It is necessary to conclude that the radiation theory is insufficient to explain the activation of molecules in homogeneous reactions of first order."

But an experimental test of radiation effect in these cases could remain without results: first a sufficiently powerful radiational flux on an elementary volume of the medium is necessary for the activation of molecules by irradiation (see below); secondly because a corresponding

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radiation absorption coefficient of the medium is necessary. This coefficient varies inversely proportional to the concentration and therefore at weak particularly concentrations of the reacting molecules of the substance the radiation effect may easily escape experimental observation.

Without further criticism of the radiative theory of activation the existence of a wide class of photochemical reactions should be first mentioned (3, 4). Besides this, a number of other reactions excited by radiative energy of some frequency (5, 6) occurs. Finally, it is known that in burning reactions water vapor ( $H_2O$ ) and some other gases, for instance nitrogen dioxide ( $NO_2$ ), have the absorption band in the near infrared region of the spectrum (7) which considerably accelerates the combustion (8, 9) as soon as they are added to the mixture. In connection with the last circumstance it is proper to express some opinions.

In his book "The Chain Reaction" N. N. Semenov (8) writes: "A whole series of specific admixtures effects the flash point and the velocity of reaction of the explosive mixture ( $H_2 + O$ ), the most astonishing being the effect of  $NO_2$ ". In the book "Combustion, Flame and Explosions in Gases" Lewis and von Elbe (9) state: "... small traces of nitrogen dioxide remarkably affect the reaction of hydrogen with oxygen". V. N. Kondrat'yev remarks in his monograph "Spectral Study of Chemical Gas Reactions" (10): "If some doubts exist on the possibility of flashing absolutely dry mixtures of carbon dioxide by forced spark ignition and high pressures, the burning of such mixtures under ordinary flame conditions should be considered entirely impossible."

Of course every researcher will explain this phenomenon along his line, based on these or other representations of the reactive mechanism, but the experimentally detected facts of strong effect of admixtures on the reaction process could also be used as basis for the radiative theory of reaction excitement.

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According to the order of magnitude of the activation energy of molecules in the burning reaction of gaseous air mixtures, the active photons should correspond to the frequency near the infrared region of the spectrum. In Table 3 are compiled the known wave lengths and frequency bands of absorption near the infrared part of the water vapor spectrum ( $H_2O$ ) and the values of photon energy corresponding to these bands. The same table shows the known band A of intense absorption of solar radiation by atmospheric oxygen ( $O_2$ ). This band is located on the boundary of the red and infrared spectrum bands (see Table 3 in the appendix).

As seen from data of this table, the energy of photons absorbed by water vapor in the near infrared of the radiation spectrum corresponds in order of magnitude to the required values of activation energy necessary for excitation of the burning reaction in inflammable gaseous mixtures.

Table 4 contains the mean values of kinetic energy of the shifted molecules for various temperatures. The same table shows also the number of molecules the input kinetic energy of which exceeds the conditionally accepted activation energy  $E = 30\,200$  kcal/kg mol. These data show that at a gas temperature  $0^\circ$  of the total number of molecules  $26.8 \times 10^{24}$  in  $1\text{ m}^3$  only an average of 17 molecules may possess an energy above  $30\,200$  kcal/kg mol (see Table 4 in the appendix).

The independent development of the burning reaction under such conditions is practically out of question. At a temperature of  $1000^\circ$  the number of molecules with an energy exceeding  $30\,200$  kcal/kg mol will average about 15 molecules per million. This number of active molecules appears to be more than sufficient to secure an independent burning reaction. In this way the initial artificial excitation of molecules in the insufficiently heated inflammable mixture may initiate a further spontaneous heating from started burning reactions. For the evaluation of the sufficiency of the thermal state of the inflammable mixture necessary for the spontaneous self-development of the burning reaction, the knowledge of the flash point may be helpful.

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### 3. HEATING OF THE INFLAMMABLE MIXTURE BEFORE ITS GENERAL INFLAMMATION

By a comparatively simple computation of heat transfer from the burning zone into the zone of inflowing inflammable gaseous mixture one may show that in the process of heating the mixture up to its flash point heat transfer plays a rather insignificant role in comparison with the heat emitted by excited reactions. For this purpose let us consider the following simplified scheme of the process of flame propagation (Figure 5).

The zone of combustion products consists of a flat parallel layer of limited width and unlimited surface, homogeneously heated to a temperature of  $t_{ph}$ . The fresh burning mixture flows to the combustion front from unlimited space with a uniform velocity  $w_0$ ,  $\text{nm}^3/\text{m}^2\text{hr}$ . The mixture contains more or less water vapor and therefore is ray-absorptive. Because the molecular heat transfer from the combustion front towards the inflowing mixture plays such a small role in comparison with the radiative transfer, the author assumes that basically the mixture is heated on account of absorption of radiative energy emitted by the combustion front. In the case of a one-dimensional diagram of flow the equation for the determination of the flame velocity of the burning mixture may be written in the form

$$w_0 c_p t_0 - w_0 c_p t_1 = q_{\text{ray}} \quad (8)$$

The radiative heat transfer may be computed from the equality

$$q_{\text{ray}} = \epsilon_{ph,f} (\vartheta_{ph} - \vartheta_f)$$

where  $\epsilon_{ph,f}$  is the conditional opacity coefficient at radiative exchange between the zones of burning products and the heated burning mixture,

$\vartheta_{ph} = 1.9 \left( \frac{T_{ph}}{100} \right)^4$  and  $\vartheta_f = 1.9 \left( \frac{T_f}{100} \right)^4$  are the superficial densities of radiation of a perfect black body at temperatures  $T_{ph}$  and  $T_f$ .

[\*NOTE: The letter "n" possibly stands for "nagretyy" which means "heated"; thus  $\text{nm}^3/\text{m}^2\text{hr}$  would mean a unit of velocity for some heated gas.]

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For the determination of the flame velocity we have the expression

$$w_0 = \frac{\varepsilon_{ph,f} (\vartheta_{ph} - \vartheta_f)}{c_1 t_f - c_2 t_1} \quad (9)$$

The radiative heat transfer of combustion products behind the burning front to the surrounding medium lowers the temperature from its theoretical value  $t_d$  to  $t_{ph}$  (d stands for degree). Hence we have the equality

$$w_0 c_1 t_d - w_0 c_2 t_{ph} = \varepsilon_{ph,o} (\vartheta_{ph} - \vartheta_o) \quad (10)$$

where  $\varepsilon_{ph,o}$  is the conditional opacity coefficient at radiative exchange between the zone of combustion products and the cooling medium and  $\vartheta_o = 4.9 \left( \frac{T_o}{100} \right)^4$  is the superficial density of radiation of a perfect black body at temperature  $T_o$ .

From equations (9) and (10) we obtain by eliminating  $w_0$  an equation for the determination of the temperature of the combustion front

$$\frac{c_1 t_d - c_2 t_{ph}}{c_1 t_f - c_2 t_1} = \frac{\varepsilon_{ph,o} (\vartheta_{ph} - \vartheta_o)}{\varepsilon_{ph,f} (\vartheta_{ph} - \vartheta_f)} \quad (11)$$

If  $\vartheta_o \ll \vartheta_{ph}$  and  $\vartheta_f \ll \vartheta_{ph}$  and  $\varepsilon_{ph,o} \approx \varepsilon_{ph,f}$  we have

$$c_1 t_{ph} = c_1 t_d - (c_1 t_f - c_2 t_1) \quad (12)$$

Under these conditions the temperature of the combustion front will be the higher, the higher the theoretical temperature of combustion  $t_d$ , the lower the flash point  $t_f$  and the higher the initial temperature  $t_1$ . According to equation (9) the propagation velocity of the flame will be the higher, the higher the temperature of the combustion front.

Computations of flame velocity according to equation (9) for inflammable mixtures of CO and  $H_2$  with air at stoichiometric composition for the mixture at  $t_1 = 0$  and for various widths of layers of combustion products give the results shown in Table 5.

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Table 5 contains also experimentally-found maximum values of the normal flame velocity at room temperature and at pressure  $p = 1 \text{ atm}$  (11).

Comparing the computed value of the flame velocity of inflammable mixtures of CO and  $\text{H}_2$  with air with the experimentally-found value, the author finds that for limited widths of flame layers the experimental value  $w_0$  appears to be much higher. The usual simplifications of computation of the flame velocity according to the scheme <sup>of</sup> increased thermal conductivity cannot explain the lower value obtained. The heating of the inflammable mixture by the walls of the tube during the experimental determination of flame velocity consists in a secondary heat transfer by radiation because the walls receive the radiant heat from the combustion products. Missing is the heat transfer by turbulent thermal conductivity in a laminar flow, conditions under which the flame velocity is usually measured.

Thus it may be assumed that the only cause for the accelerated heating of the inflammable mixture to the temperature of its flash point is the heat emitted by the reactions excited by the inflow of inflammable mixture.

#### 4. DETERMINATION OF THE VELOCITY OF FLAME PROPAGATION BY PHOTON ACTIVATION OF MOLECULES

Assuming that the inflammable mixture is basically heated before inflammation mainly because of reactions excited during absorption of photons released by the combustion front, under conditions of the above discussed scheme, one can determine the velocity of flame propagation.

The equation of energy balance in an elementary portion of displacement of the inflammable mixture in front of the combustion front for the above-mentioned simplifying assumptions may be written in the form

$$- w_0 c_p dT = q_x dx \quad (13)$$

where  $c_p$  is the heat capacity of the heated mixture at constant pressure in kcal/m<sup>3</sup>deg and  $q_x$  is the heat emitted in kcal/m<sup>3</sup>hr per unit volume from excited reactions of the irradiated inflammable mixture.

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The value  $q_x$  may be considered proportional to the intensity of irradiation absorbed per unit volume ( $\int_{4\pi} k I_{p,x} d\omega$ ), to the factor  $e^{-E_a/RT_x}$  and to the thermal effect  $Q$  of the reaction. Hence we have

$$q_x = CQe^{-E_a/RT_x} \int_{4\pi} k I_{p,x} d\omega \quad (14)$$

where  $C$  is a value depending on the concentration and the composition of the inflammable mixture and  $k$  is the coefficient of absorption of active photons (1/m).

If we assume that the active photons emitted by the combustion front enter the considered element of volume only from the side of the combustion front and with a uniform intensity along the whole half spatial angle  $2\pi$  (see Figure 5) the absorption of active photons will be determined by the factor  $2\pi k I_x$ .

If the intensity of the radiation emitted from the side of the combustion front is  $I_0$ , then at any point distant  $x$  from the combustion front we have

$$I_x = I_0 e^{-kx}$$

For these conditions the equation (13) may be written in the form

$$-w_0 c_p dT = CQ2\pi k I_0 e^{-kx} e^{-E_a/RT} dx \quad (15)$$

Separating the variables, we have

$$-w_0 c_p e^{E_a/RT} dT = CQ2\pi k I_0 e^{-kx} dx \quad (15')$$

Because the temperature of the flash point of most inflammatory mixtures is much lower than the theoretical combustion temperature, during the heating time of the inflammable mixture to the temperature of flash point  $T_f$  the value  $C$  in equation (15'), depending on concentration, may in first approximation be considered as invariable. Moreover, considering  $w_0$ ,  $c_p$  and  $k$  as constants, we find by integration of (15') that

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$$\omega_0 c_p \left\{ T_i e^{E_A/RT_i} - T_f e^{E_A/RT_f} - \frac{E_A}{R} \left[ \ln \frac{T_i}{T_f} + \left( \frac{E_A}{RT_i} - \frac{E_A}{RT_f} \right) + \right. \right. \\ \left. \left. + \frac{(E_A/RT_i)^2 - (E_A/RT_f)^2}{2 \cdot 2!} + \frac{(E_A/RT_i)^3 - (E_A/RT_f)^3}{3 \cdot 3!} + \dots \right] \right\} = \\ = C Q 2 \pi I_0 (1 - e^{-KL}) \quad (16)$$

If  $T_i$  and  $T_f$  differ considerably, then in the left side of equation (16) a number of terms of the infinite series may be neglected; keeping only the two first terms without effecting the accuracy of the equation, we may write:

$$\omega_0 c_p (T_i e^{E_A/RT_i} - T_f e^{E_A/RT_f}) = C Q 2 \pi I_0 (1 - e^{-KL}) \quad (16')$$

Hence for the velocity of flame propagation we get the equation

$$\omega_0 = \frac{C 2 \pi Q I_0 (1 - e^{-KL})}{c_p (T_i e^{E_A/RT_i} - T_f e^{E_A/RT_f})} \quad (17)$$

According to the expression obtained the velocity of flame propagation should increase: 1) with intensity  $I_0$  of irradiation of the inflammable mixture; 2) with initial temperature  $T_i$  of the mixture; 3) with decrease of flash point  $T_f$ ; 4) with decrease of the activation energy  $E_A$ ; 5) with the decrease of the heat capacity  $c_p$  of the heated mixture; 6) with absorption coefficient  $k$  and length of radiation path. This characteristic effect of the factors outlined above on the velocity of flame propagation agrees with the available experimental material.

If the absorption coefficient  $k$  of the inflammable mixture is close to zero, then the velocity of flame propagation will tend to zero too; such a mixture therefore is difficult to ignite by radiation. The incombustibility of a perfectly dry mixture of carbon dioxide with air may serve as an example.

The irradiation intensity  $I_0$  of an inflammable mixture emanating from the combustion front depends on the composition of combustion products formed

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and on their temperature. The effect of temperature on irradiation intensity is rather strong, and in this connection the velocity of flame propagation also will mostly depend on temperature.

Under conditions of thermodynamic equilibrium the radiation intensity is determined by the expression

$$I_{\nu T} = 0.93 \cdot 10^{-42} \frac{E_{\nu}^3}{e^{E_{\nu}/RT}} \text{ kcal/m}^2 \text{ hr} \cdot \text{steradian} \quad (18)$$

Figure 6 shows the behavior of the curves  $I_{\nu T} = f(T)$ , which proves that with decrease of temperature the intensity of equilibrium radiation drops very rapidly. For <sup>the</sup> disequilibrium state the radiational flux emanating from the combustion front may differ considerably from the value obtained from equation (18) (see below) and in such cases luminiscence may appear more or less pronounced within the flame.

The theoretical combustion temperature of gas and air mixture depends on the concentration of the inflammable gas in the mixture. Table 6 and Figure 7 present, versus concentration, the theoretical combustion temperatures, computed without taking the dissociation into account, for gas and air mixtures of CO, H<sub>2</sub> and CH<sub>4</sub>. The theoretical combustion temperatures, corresponding to the stoichiometric mixture composition, are noted in Table 6 separately. For such a mixture the highest theoretical combustion temperature is obtained.

If the luminiscence of the combustion products does not play a decisive role in the excitation of the combustion reaction and the velocity of flame propagation is mostly determined by thermal radiation, we may assume that the velocity of flame propagation will follow the varying behavior of theoretical combustion temperature. Figure 7 shows for comparison the curves describing velocities of flame propagation in gas and air inflammable mixtures of CO, H<sub>2</sub> and CH<sub>4</sub> according to experimental data (12).

As is seen, the behavior of curves describing velocities of flame propagation corresponds in the first approximation to the variable behavior of the theoretical combustion temperature.

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## 5. RADIATIVE PECULIARITIES OF COMBUSTION PROCESSES

In combustion processes, a noticeable deviation from local radiative equilibrium ( $I'_v \neq I_{v,T}$ ) may occur because of kinetic peculiarities of proceeding processes, and in such cases the radiative output will differ from the thermodynamic radiative equilibrium.

In the general case the energy balance (if we neglect the non-essential terms) will be determined by the following equation

$$\int_{4\pi} d\omega \int_0^\infty \kappa_v I'_v dv = \int_{4\pi} d\omega \int_0^\infty \kappa_v I_{v,T} dv - [q_v + \text{div}(\lambda \cdot \text{grad } T) - \frac{D(c_p \gamma T)}{d\tau} + A \mu \text{diss } F(\omega) + A \frac{Dp}{d\tau}] \quad (19)$$

where  $q_v$  is the productivity of sources of heat output per unit volume;  $\text{div}(\lambda \cdot \text{grad } T)$  is heat influx by molecular energy transfer;  $\frac{D(c_p \gamma T)}{d\tau}$  is total variation of heat content per unit volume in time;  $A \mu \text{diss } F(\omega)$  is the heat influx from dissipation of energy of displaced masses ( $\mu$  is the viscosity coefficient,  $\text{diss } F(\omega)$  is the dissipative function,  $A$  is the thermal equivalent of work),  $A \frac{Dp}{d\tau}$  is the complete change of pressure per unit volume.

The intensity  $I'_v$  of the radiation may vary depending on the productivity of sources of thermal efflux outflow, of molecular energy transfer and the total variation of heat content and pressure in the volume and also on the absorption coefficient  $k$ .

For the whole spectrum, the average intensity of radiative emission from unit volume is found from the equation

$$\bar{I}' = \bar{I}_T - \frac{1}{4\pi k} [q_v + \text{div}(\lambda \cdot \text{grad } T) - \frac{D(c_p \gamma T)}{d\tau} + A \mu \text{diss } F(\omega) + A \frac{Dp}{d\tau}] \quad (20)$$

where  $k$  is the mean absorption coefficient.

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With increase of combustion velocity the productivity of thermal sources increases and for other conditions equal the intensity of radiative emission should decrease. This conclusion agrees well with measured data of radiation in flames, processed by V. E. Garner, <sup>(13)</sup> who found that with increase of velocity of flame propagation the intensity of its radiation decreases. V. E. Garner supposed here that a part of the radiation consists in luminescence.

Table 7 presents the results of Garner's measurements <sup>(8)</sup> on the effect of water vapor on the intensity of radiation and the velocity of flame propagation.

As may be seen from the data of the table, an admixture of water vapor in the amount of 2% produces a 10-fold increase of the combustion velocity of the inflammable mixture and lowers the emission of radiation nearly 4-fold. Because here the absorption coefficient of the inflammable mixture is proportional to the concentration of water vapor, the four-fold decrease of radiative emission for a 10-fold increase of combustion velocity cannot be considered as contradictory to the above stated radiative theory of excitation of combustion reaction. The combustion velocity is proportional to the product of radiative intensity and the absorption coefficient of the inflammable mixture, which for presence of water vapor has a much steeper rise than the drop of radiative intensity.

It should be noticed that the decrease of intensity of total radiation, a considerable part of which has a thermal origin, does not mean a decrease of photon radiation which excite the reactions. With decrease of total radiation, the "active" radiation may even increase.

The emission of radiation during combustion reactions is determined by the liberation of energy in elementary acts, and an essential part of this process may be radiation of energy of relatively high quanta. For instance, the luminescence of CO flame as typical blue glow is well known <sup>(10)</sup>. The luminescence of solids in flame is also known <sup>(11)</sup>.

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Besides this kind of instability near the combustion front at the side of an inflowing inflammable mixture, an instability between the "molecular" and "radiative" temperatures exists. The instability in the region of an inflowing inflammable mixture will be higher the higher the irradiation of an elementary volume at the side of the combustion front. In order to illustrate the various types of irradiation of an elementary volume at the side of the incandescent zone, Figure 8 represents several possible cases of distribution of radiation intensity of an elementary volume.

The case "a" corresponds to an even irradiation of an elementary volume of the inflammable mixture from the side of the combustion front with infinite surface.

The cases "b" and "c" correspond to the irradiation of an elementary volume of the inflammable mixture from the combustion front with a limited surface, when the intensity of irradiation is distributed proportionally to  $\cos \varphi$  and  $\cos^2 \varphi$ .

The case "d" corresponds to the irradiation of the inflammable mixture in a rather small channel.

The case "e" corresponds to the irradiation of the inflammable mixture if the combustion front has a convex shape.

The cases "f" correspond to the irradiation of an elementary volume of the inflammable mixture which entered immediately into the chamber with incandescent walls and was irradiated from all sides.

All these cases of irradiation of the inflammable mixture in an elementary volume correspond more or less to real conditions of the combustion process.

The highest "radiative" temperature in an elementary volume will correspond to the case "f", and the lowest to the case "c". Because of the great penetrating power of photons in comparison to molecules, the gradient of "radiative" temperature for cases approaching "a" and "f" will appear to

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be considerably less than the gradient of "molecular" temperature. Under such conditions the number of active photons, penetrating the envelope of an elementary volume will appear to be many times greater than the number of active molecules conveyed to the elementary volume toward the inflowing inflammable mixture.

The decrease of the velocity of flame propagation with decrease of irradiation of the inflammable mixture finds confirmation in the familiar experimental fact that velocity of flame propagation decreases with decrease of pipe diameter. In pipes of very small diameter the combustion of the inflammable mixture is extinguished.

If the combustion front is separated from the inflammable mixture flowing in by a sufficiently dense screen, then the flame propagation toward the inflowing mixture, as is known, ceases, even if the inflammable mixture has a low flash point. The stopping of flame propagation by means of screens has been long applied to prevent explosions of inflammable mixtures.

A role similar to the screen may be performed by incombustible dust, present as an admixture in the inflammable gaseous mixture. As shown by the experiments of A. S. Predvoditelev and S. I. Gribkova <sup>(15)</sup> the presence of incombustible dust of silica gel (dimensions of dust particles 12 to 2 microns) in the inflammable mixture of CO with air leads to a decrease of the velocity of flame propagation. The indicated velocity drops with increase of dust condensation and also decreases the more the smaller the dimensions of the dust particles. The decrease of the velocity of flame propagation in these experiments together with increase of heat capacity and lowering of combustion temperature may be ascribed to the screening effect of incombustible dust particles.

In the experiments of the same authors the accelerating effect of admixtures of combustible dust of activated charcoal was also detected (the dimensions of particles 6 to 10 microns). The finer the combustible dust

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and the stronger is concentration in the mixture of CO and air, the higher was the velocity of flame propagation. This accelerating effect of admixtures of combustible dust corresponds somewhat to the photon activation of the inflammable mixture of dust and air before its inflammation.

The strongest irradiation of the inflowing inflammable mixture in an elementary volume will be reached under conditions approaching case "f". This case corresponds to the so-called flameless gas combustion.

If we place in the zone of the combustion front a ceramic nozzle, it will, after getting heat by convection from the incandescent combustion products, emit the heat thus increasing the irradiation of the fresh inflammable mixture flowing in. This method of intensification of combustion is widely applied in industry (16, 17).

If under the conditions of the combustion process the material of the nozzle is able to emit in the chemically active spectral band a non-temperature (nonthermal) radiation of intensity higher than the radiation of the perfect black body at the same temperature, then the flame velocity of the inflammable mixture may still be increased. In this respect refractory materials having a so-called cando-luminiscence are of interest (18).

Some of these materials, located in a flame, as, e.g. oxides of MgO, CaO,  $ZrO_2$  and other have the property, depending on temperature, to emit radiation in a certain spectral band 10-fold and even 100-fold stronger than the radiation of a perfect black body at the same temperature. This kind of radiation occurs only if the substance is within the flame, while this kind of glow occurs in the zone of association of oxygen and hydrogen and in lesser degree with hydrocarbons.

The emission of non-thermal radiation under these or other conditions agree with equation (19), which is one of the most important equations for combustion processes.

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The investigation of non-temperature radiation in the chemically active spectral band will facilitate the explanation of the role of the positive catalysts in the combustion process. It is necessary to develop experimental work along this line.

## CONCLUSIONS

1. Comparison of the distribution of radiative and kinetic energies among carriers in an elementary volume showed that photons at high energy levels have relatively heavier statistical weight than gas molecules at the same energy.
2. It was shown that under corresponding conditions the probability of photon activation of inflammable mixtures may be considerably higher than the probability of activation for the case where molecules collide. The most important role in this case pertains to radiative absorption of admixtures of the inflammable mixtures.
3. It was determined by computation that in the heating process of inflammable mixtures before the flash point the main role is played by thermal emission from reactions excited in inflowing inflammable mixtures by photon activation.
4. An equation for the determination of the velocity of flame propagation for the case of photon activation of molecules is obtained, which, according to the effects of individual factors, agrees completely with experimental data.
5. Using the equation of energy balance as a basis, the author succeeded in showing the peculiarities of the combustion process under various conditions. He noted the role of the nonequilibrium radiation before the flash point of inflammable mixtures as well as in the combustion process.

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Table 1

t = 0	500	1000	1500	2000°C
T = 273	773	1273	1773	2273°K
$N_A/N_{ph} = 6.5 \cdot 10^9$	$101 \cdot 10^6$	$13.7 \cdot 10^6$	$3.63 \cdot 10^6$	$1.35 \cdot 10^6$

Table 2

t = 0	500	1000	1500	2000°C
$E_{30\ 200}/RT = 55.7$	19.7	11.9	8.58	6.7
$n_{E_y}/n_{E_1} = 154$	32.3	15.1	9.27	6.38
$n_{>E_y}/n_{>E_1} = 1335$	179	70	38.6	25.1

Table 3

Indexes	H <sub>2</sub> O						O <sub>2</sub> A band
Wave length $\lambda, \mu$	0.72	0.944	1.128	1.367	1.843	2.75	0.76
Frequency of radiation, $\nu \cdot 10^{-13} 1/\text{sec}$	41.6	31.7	26.5	21.9	16.2	10.9	39.4
Energy of photon, $E_{ph} = h \cdot \nu \cdot 10^{-13} \text{ erg}$	27.6	21	17.5	14.5	10.7	7.22	26.1
Energy of photon $E_{ph}$ electron-volt	1.72	1.31	1.095	0.908	0.67	0.451	1.63
Quantum energy of mol, $E_{ph} = N_{E_{ph}} \text{ kcal/kg mol}$	39 600	30 200	25 250	20 950	15 450	10 400	37 600

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Table 4

Temperature, °C	0	500	1000	1500	2000
Mean energy of shifting of molecule $\bar{E}_M \cdot 10^{13}$ erg.	0.565	1.6	2.635	3.67	4.7
Mean energy of shifting of molecule $\bar{E}_M$ , kcal/kg mol.	813	2300	3790	5280	6770
Amount of Molecules with energy $\bar{E}_M > 30\ 200$ kcal/kg mol: $(-\ln n_M)$ .	55.7	19.7	11.9	8.58	6.7

Table 5

Inflammable mixture	$t_f$	$t_d$	$t_{ph}$	Width of layer of combustion products				Experimentally found propagation velocity of flame $w_o$ , $\frac{\text{nm}^3}{\text{m}^2 \text{ sec}}$
				$s = 2 \text{ cm}$		$s =$		
				$E_{ph}, f$	$\frac{W_o}{\text{nm}^3/\text{m}^2 \text{ sec}}$	$E_{ph}, f$	$\frac{W_o}{\text{nm}^3/\text{m}^2 \text{ sec}}$	
CO + air ( $\alpha = 1$ )	650	2370	1930	0.02	0.03	0.2	0.3	0.415
H <sub>2</sub> + air ( $\alpha = 1$ )	550	2240	1850	0.008	0.0124	0.43	0.667	2.67

[\* Note: as already mentioned in a previous footnote,  $\text{nm}^3/\text{m}^2 \text{ sec}$  is possibly a unit of velocity for heated gases, where "n" stands for "nagretyy" meaning "heated".]

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Table 6

<u>Mixture of CO and air</u>												
Concentration CO, %	20	25	29.6	35	40	45	50	55	60	65	70	
Theoretical combustion temperature, $t_g^{\circ}$ , C	1680	2050	2370	2215	2065	1910	1750	1605	1440	1275	1110	
<u>Mixture of <math>H_2</math> and air</u>												
Concentration of $H_2$ , %	10	15	20	25	29.6	35	40	45	50	55	60	65 70
Theoretical combustion temperature, $t_g^{\circ}$ , C	805	1180	1550	1910	2240	2080	1940	1800	1650	1505	1350	1190 1030
<u>Mixture of <math>CH_4</math> and air</u>												
Concentration of $CH_4$ , %			6	7	8	9.5	11	12	13			
Theoretical combustion temperature, $t_g^{\circ}$ , C			1395	1590	1770	2040	1970	1920	1875			

Table 7

% $H_2O$	Intensity of radiation in kcal $\times 10^6$	Velocity of flame m/sec
0.00	6.00	1.00
0.23	2.75	7.80
0.44	2.39	9.00
1.95	1.63	10.00

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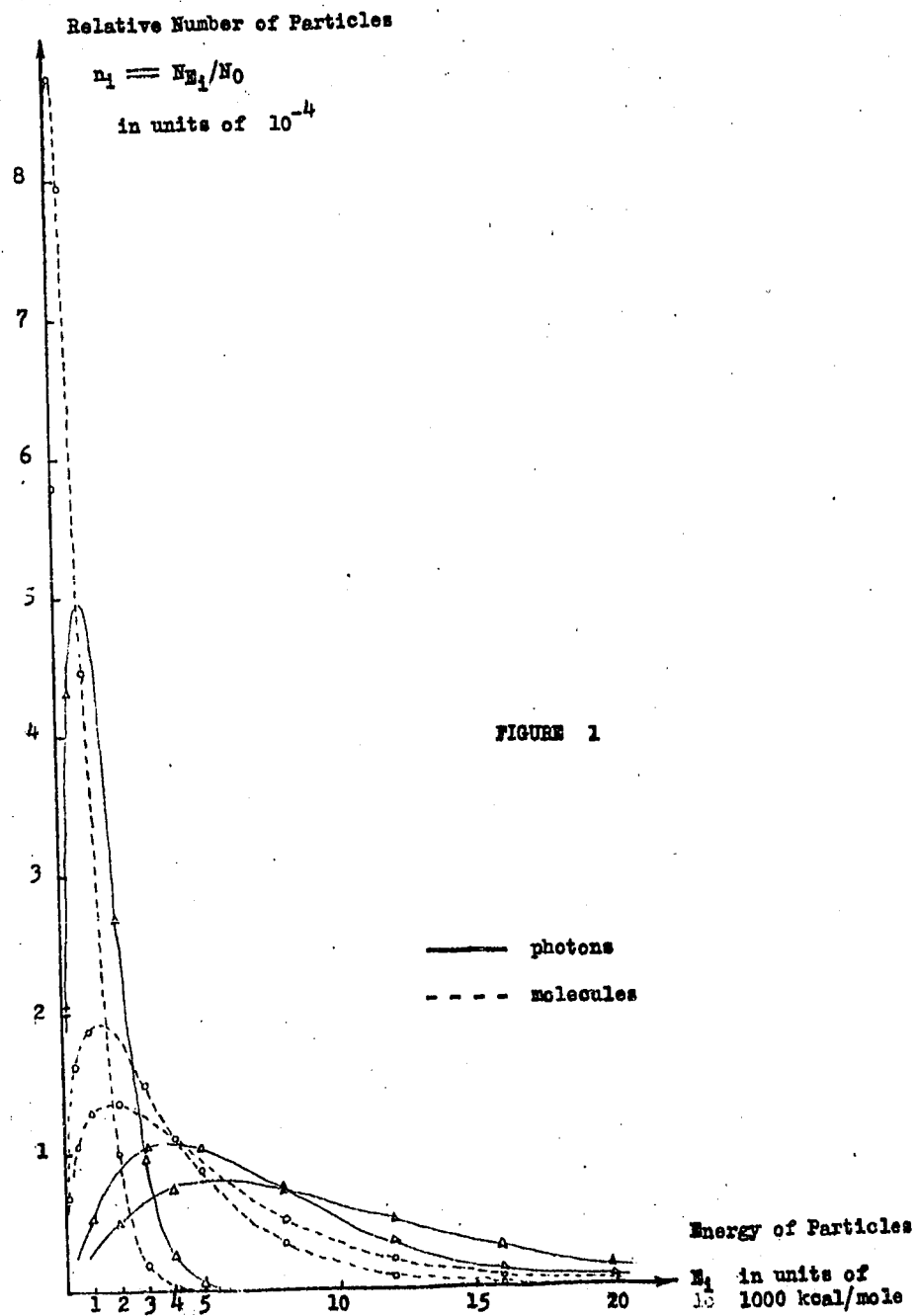
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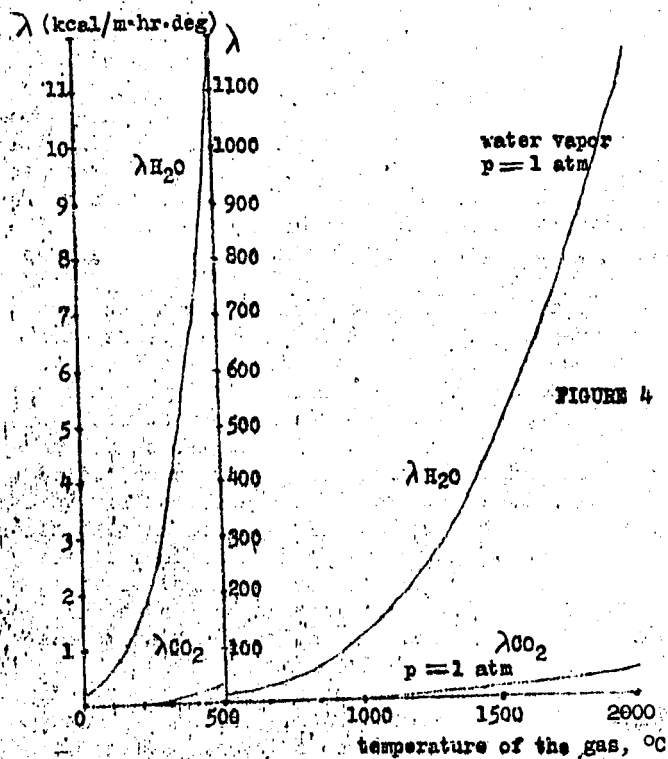
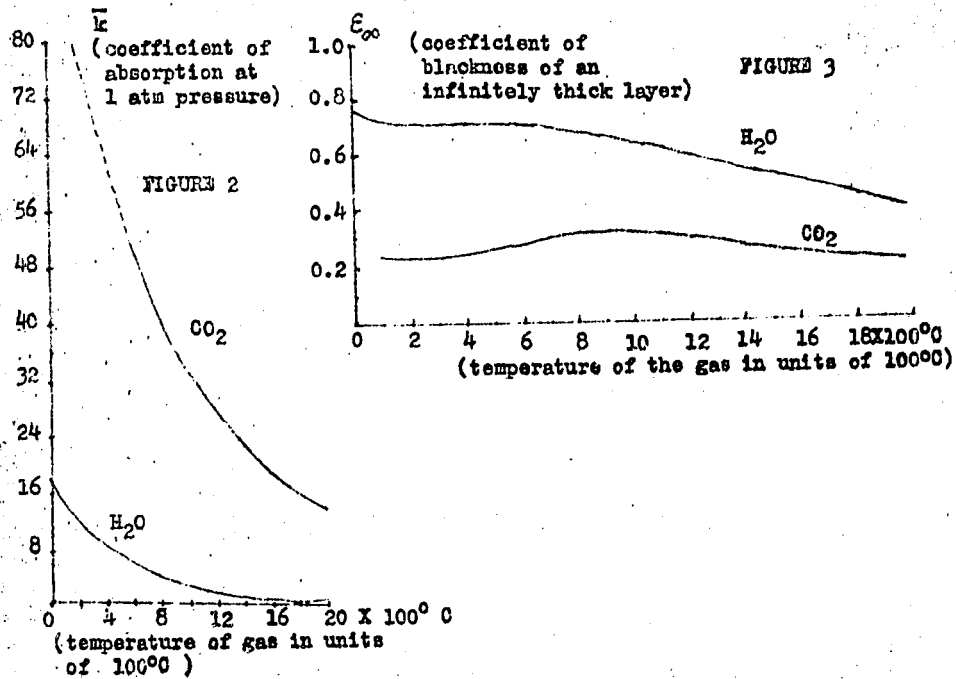
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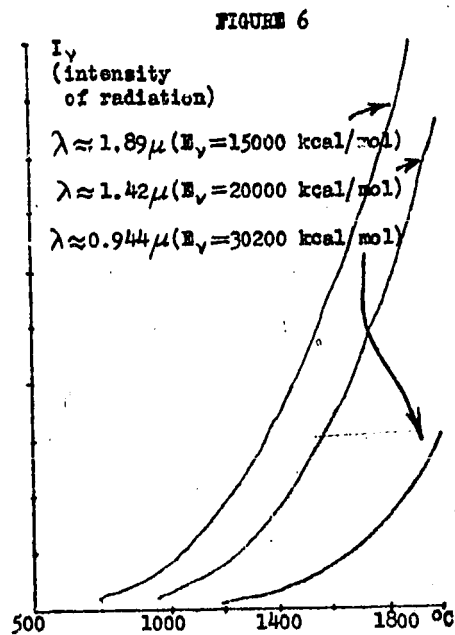
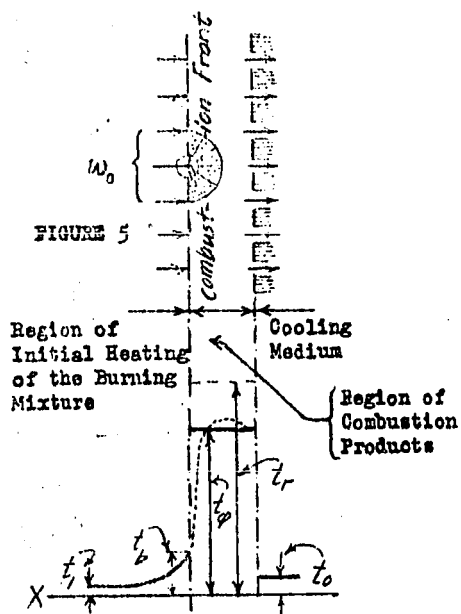
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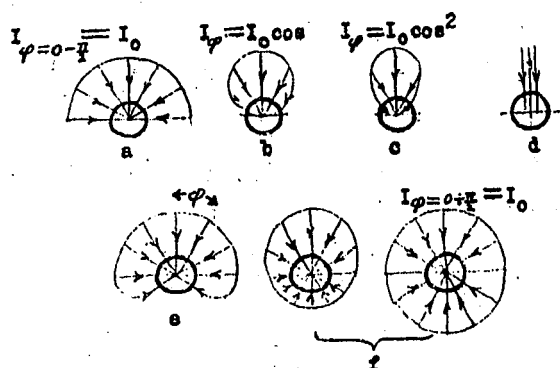
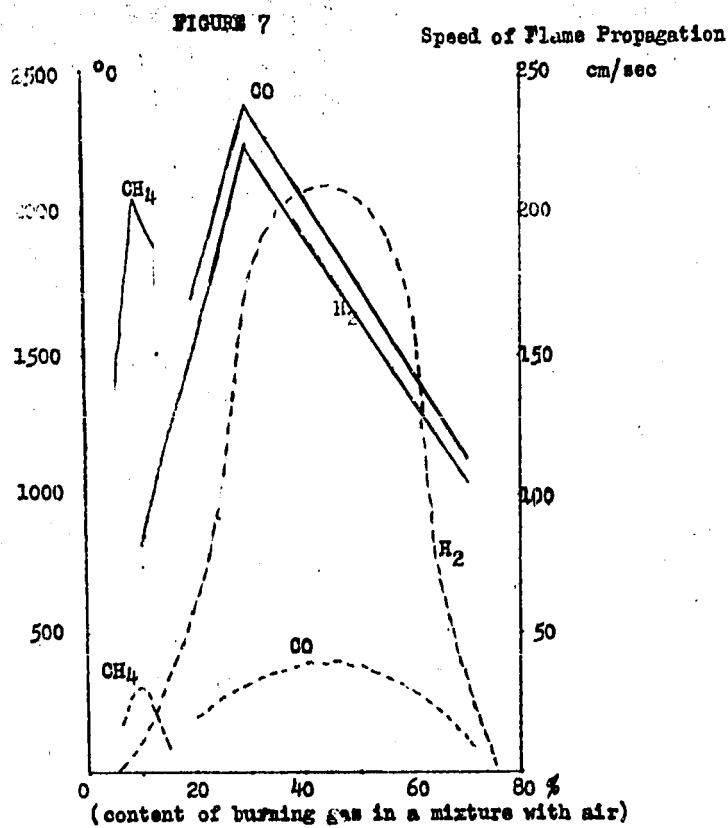


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**FIGURE 8**

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